

A Holistic Approach to Sensor and Analytical Method Development

Barry M. Wise, Neal B. Gallagher,
Richard M. Ozanich,* and Jay Grate*

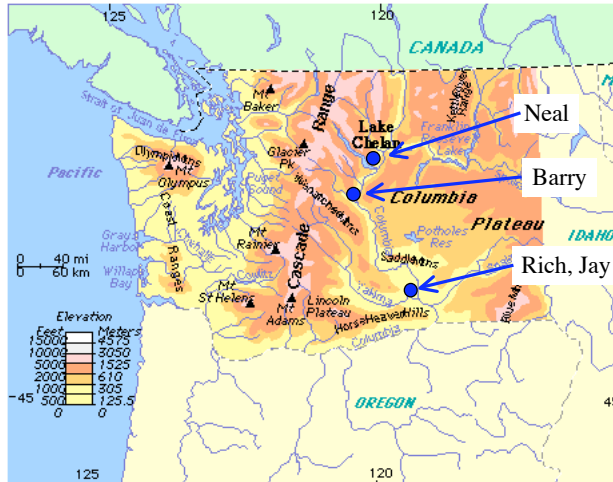
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Richland, WA USA



United States



Washington State



Outline

- Concept of holistic design
- Examples
 - Laser Photo-acoustic Spectroscopy Sensor
 - GC-Surface Acoustic Wave Sensor

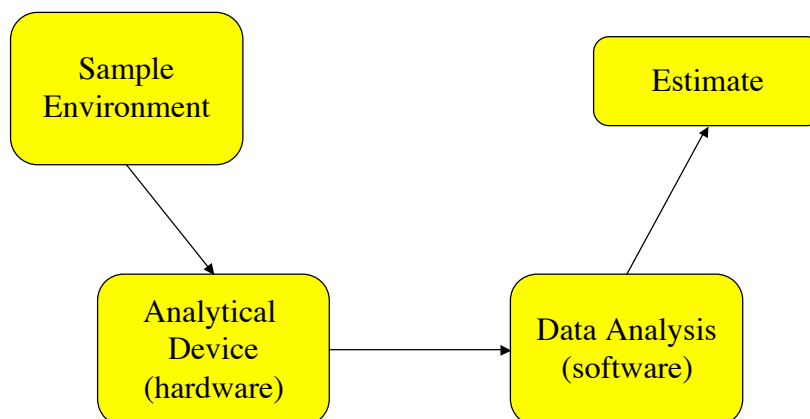


Holistic Design Concept

- Analytical systems can not be optimized one piece at a time
- Model the whole analytical system, from sample environment to output
- Lots of parts to consider



Overall Model



Sample Environment Model

- Analytes of interest
- Interferents, mean, covariance, distribution
- Specific problem interferents
- Situation specific scenarios
- Sampling error



Analytical Instrument Model

- Typically a blend of theoretical, empirical and statistical elements
- Ideal response
- Noise model
- Non-idealities
- Sensor selection



Data Analysis

- Detection, concentration, classification...
- What sort of model?
- How to calibrate?

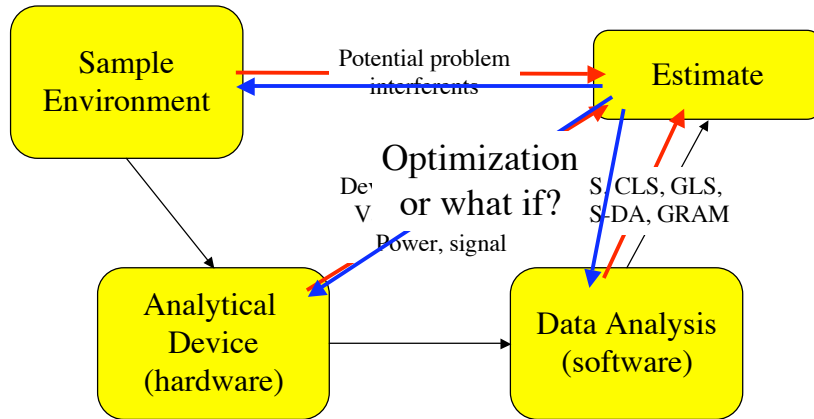


Exercising the Models

- Monte Carlo
- Can sometimes propagate theoretically
- Often interested in the distribution tails



Model Use



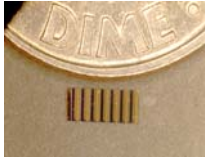
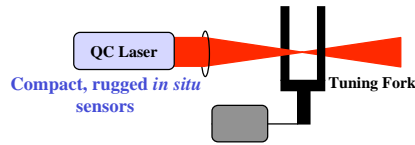
Example 1

- Laser Photo-acoustic Spectroscopy Sensor
- Detection of G-agents in battlefield scenario
- DARPA project lead by PNNL
- Reference:
 - **Laser photo-acoustic chemical sensor performance modeling**, J. F. Schultz, B. D. Cannon, T. L. Myers, R. M. Ozanich, D. M. Sheen, M. S. Taubman, M. D. Wojcik, N. B. Gallagher, B. M. Wise, **Proceedings of SPIE Vol. #57**



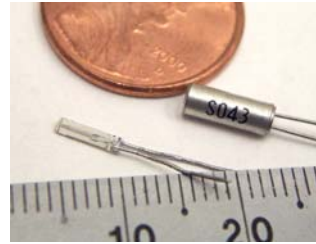
QC L-PAS Sensor Concept

Laser photo-acoustic sensors (L-PAS):



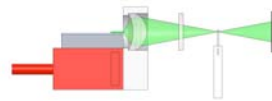
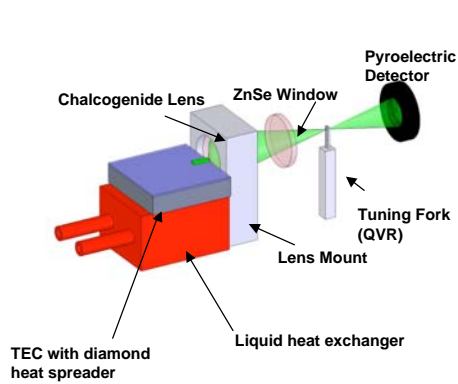
QC & IC lasers:

- Wavelengths from ~ 2 – 100 μm
- FM & AM modulation
- Small sizes for λ multiplexing
- ~10 cm^{-1} tuning per laser
- 600 mW CW @ 300 K, (6 μm)
- Repeatable, readily stabilized



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Sensor and Optics Design



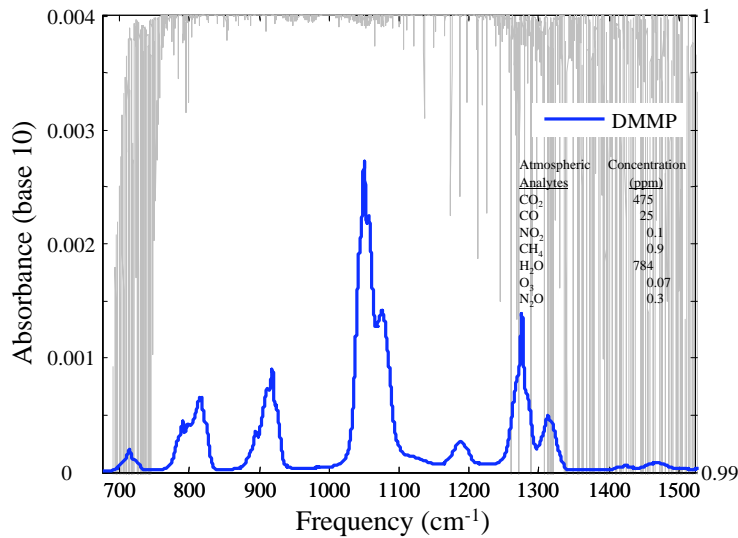
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QVR Voltage and Noise Sources

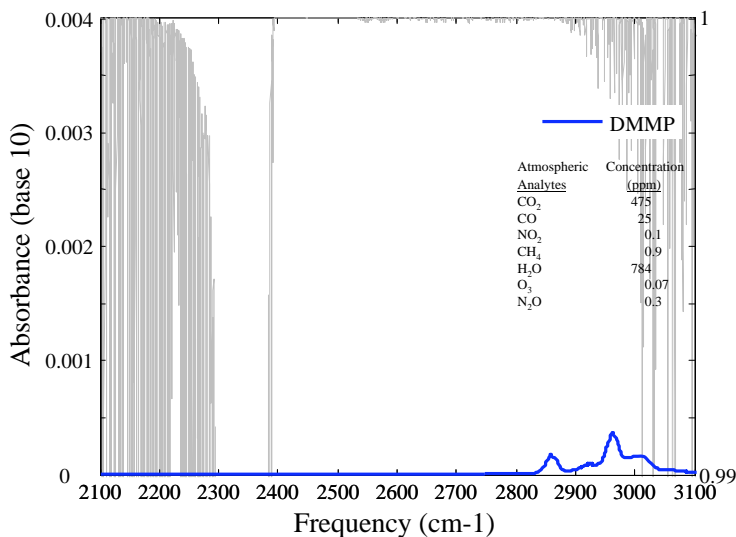
$$V_{QVR} = Z_{gain} \cdot \left(A_1 \cdot \sum_{Chem} C_{Chem} \sum_{\lambda} P_{\lambda} \cdot \sigma_{Chem,\lambda} + \sum_{Solid} A_{2,Solid} \sum_{\lambda} P_{\lambda} \cdot \alpha_{\lambda} + ThermalNoise \right)$$

- **P_{λ} –Power in QCL mode λ**
 - Varies more than total QCL power except for single mode QCL
 - Measure total QCL power to 1% relative reproducibility
- **Cross Section $\sigma_{chem,\lambda}$**
 - Varies with wavelength and hence laser line shape and laser chirp
- **Chemical Concentrations- C_{Chem}**
 - Analyte & clutter (both vary)
- **Thermal Noise in QVR**
 - Analogous to Johnson noise
 - Limits sensitivity in Rice expts.
- **Acoustic Interference at AM frequency**
 - AM laser power absorbed by QVR & other surfaces
 - Measure to generate specs for optics design
 - Variations in QCL power and coupling to QVR create noise
- **Preamp gain Z_{gain}**
- **Acoustic coupling coefficients ($A_1, A_{2,solid}$)**

Simulant Spectra in the Long-Wave IR



Simulant Spectra in the Mid-Wave IR



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Initial Design Atmosphere

- “Standard” constituents vary independently between mean values of EPA rural and urban atmospheres
- Only species with IR absorptions are listed at right
- Single-component interferences vary from 0 to max value
- Diesel exhaust constituents co-vary ($R^2=0.8$) from 0 to max values (close proximity to running diesel engine)

TA Blake, KM Probasco, “Chemical Emission Scenarios and Detection Limits for Active Infrared Remote Sensing”, PNNL Report 13382 (2000).

Analyte	Concentration (mg/m ³)
CO ₂ *	634-7065
H ₂ O	0-1163
NO ₂ *	0.0038-250
CO*	12-46
SO ₂ *	0.026-13
Formaldehyde*	0.0025-3.0
CH ₄	0.1-1.1
Toluene	0.0076-0.76
N ₂ O	0.36-0.7
Dodecane	0.014-0.49
H ₂ S	0.014-0.43
Benzene*	0.0064-0.24
Parathion	0-0.24
m-Xylene*	0.0044-0.22
Acetaldehyde*	0.0036-0.22
O ₃	0.059-0.2
DEET	0-0.16
Propionaldehyde*	0.0024-0.14
HNO ₃	0-0.065
Acrolein*	0.0023-0.06
Butadiene*	0.0022-0.038
Carbonyl Sulfide*	0.0025-0.032
NH ₃	0.00002-0.0035
HCN	0-0.0011
Ethylene Glycol	0-0.00026

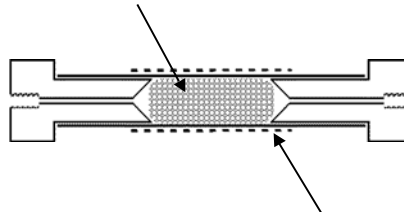
* Diesel constituent

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Pre-concentrator

Core containing solid adsorbent



Resistive Heating Wires



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Initial Design Atmosphere With Pre-concentration

Concentrations shown assume pre-concentration, resulting in 10-fold concentration of agents and the following concentration factors for interferences:

- ⁵ = 5-Fold Concentration Factor
- ¹⁰ = 10-Fold Concentration Factor
- * = Diesel Exhaust Constituent

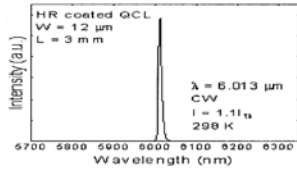
Analyte	Concentration (mg/m ³)
CO ₂ [*]	634-7065
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Formaldehyde [*]	0.0025-3.0
CH ₄	0.1-1.1
Toluene ¹⁰	0.076-7.6
N ₂ O	0.36-0.7
Dodecane ¹⁰	0.14-4.9
H ₂ S ⁵	0.07-2.15
Benzene ¹⁰	0.064-2.4
Parathion ¹⁰	0-2.4
m-Xylene ¹⁰	0.044-2.2
Acetaldehyde ⁵	0.018-1.1
O ₃	0.059-0.2
DEET ¹⁰	0-1.6
Propionaldehyde ⁵	0.012-0.7
HNO ₃ ¹⁰	0-0.65
Acrolein ⁵	0.0115-0.3
Butadiene ⁵	0.011-0.19
Carbonyl Sulfide [*]	0.0025-0.032
NH ₃ ¹⁰	0.0002-0.035
HCN	0-0.0011
Ethylene Glycol ¹⁰	0-0.0026



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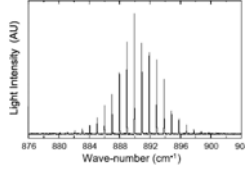
Fabry-Perot QCL Line-shapes

J. S. Yu, A. Evans, J. David, L. Doris, S. Silken, and M. Razeghi, IEEE PHOTONICS TECHNOLOGY LETTERS, VOL. 16, NO. 3, pp 747-9, MARCH 2004

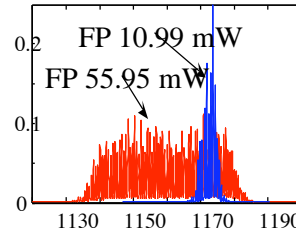


Lineshape from CW, 25 C QCL producing ~80 mW

M. Garcia a, E. Normand b, C.R. Stanley a, C.N. Ironside, C.D. Farmer, G. Duxbury, and N. Langford, Optics Comm 2003



Lineshape from 12 A, 9 ns pulsed QC laser



Lineshape from Maxion QCL, CW cryogenic operation, 56 mW

Near threshold, CW operation:

- Single mode
- Width < 3 cm⁻¹

Initial design choice

Well above threshold, 100% current modulation:

- Multiple modes
- Width ~10 cm⁻¹
- Relative mode power stability?

Well above threshold, CW:

- Multiple modes
- Width ~ 50 cm⁻¹ wide (!)
- Relative mode power stability?



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QVR Voltage and Noise Sources

$$V_{QVR} = Z_{gain} \cdot \left(A_1 \cdot \sum_{Chem} C_{Chem} \sum_{\lambda} P_{\lambda} \cdot \sigma_{Chem,\lambda} + \sum_{Solid} A_{2,Solid} \sum_{\lambda} P_{\lambda} \cdot \alpha_{\lambda} + ThermalNoise \right)$$

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Noise Model for QC L-PAS Initial Design

$$V_{QVR} = Z_{gain} \cdot \left(A_1 \cdot \sum_{Chem} C_{Chem} \sum_{\lambda} P_{\lambda} \cdot \sigma_{Chem,\lambda} + \sum_{Solid} A_{2,Solid} \sum_{\lambda} P_{\lambda} \cdot \alpha_{\lambda} + ThermalNoise \right)$$

- Proportional noise due to QCL power variations
 - 1% relative noise using power measurement
- Additive thermal noise
 - R_{QVR} from Rice and dominated by QVR losses to the air at 1 atm.
- Neglect background from solids
 - Assumes good optics so laser beam clears QVR
 - Weak coupling of distant acoustic sources to QVR
- Neglect variations in laser chirp

$$\begin{aligned} Thermal\ Noise &= Z_{gain} \sqrt{\frac{4kT}{R_{QVR}} \Delta f} \\ &= 10M\Omega \sqrt{\frac{4k \cdot 300^{\circ}K}{90k\Omega} \cdot 0.1Hz} \\ &= 1.4\mu V(rms) \end{aligned}$$



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Laser Line Selection Using Partial Least Squares Discriminant Analysis (PLS-DA)

1. Generate synthetic data with and without agent:
 - Use 500 null spectra (clutter plus interferences plus noise) and 125 positive spectra (clutter plus interferences plus noise plus signal) for each G-agent, with concentrations ranging from 0.02-0.1 mg/m³.
 - Repeat null spectra and G-agent spectra creation 20 times to check for consistency of regression vector produced from PLS-DA (below)
2. Calculate a regression vector **b** which is the PLS best fit solution to the equation

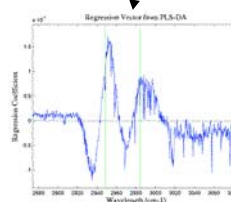
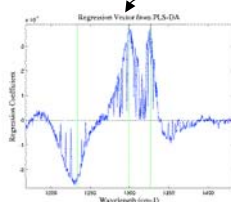
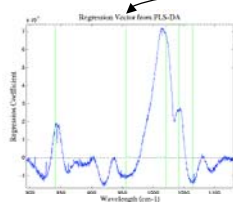
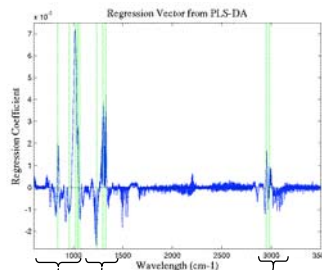
$$\mathbf{X} \mathbf{b} = \mathbf{y},$$
 where X is a matrix of the synthetic spectra, and y is a vector that classifies each spectrum as positive or null.
3. Plot **b** and select laser lines that contain the most information.



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Laser Line Selection

- Select laser lines based on regression coefficients from regression vector
 - Positive peaks correspond to agent features
 - Negative peaks account for overlapping interferences
 - Select lines with large (+/-) coefficients
 - Choose lines $>20\text{ cm}^{-1}$ apart and where regression coefficients don't change rapidly to allow for broader laser lines and drift
 - Choose lines on separate features to provide unique information



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Calculation of ROC Curves

To generate one point on a ROC curve, a specific agent concentration and defined false negative rate are chosen. For this example, a 5% false negative rate was chosen (represented by the 95% PD – vertical green line).

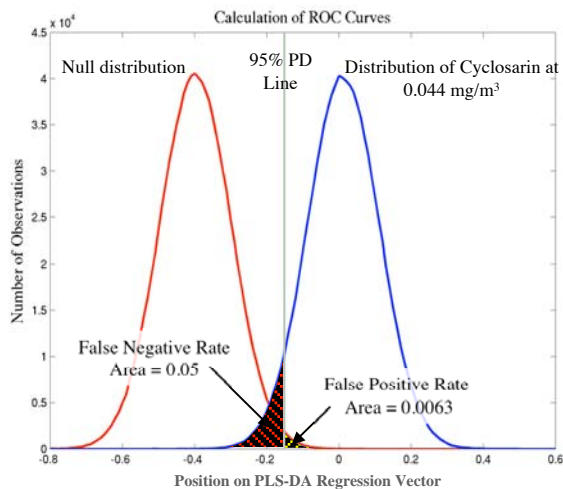
1 million spectra with and without agent were generated.

The red curve represents the values of y calculated from distribution of the samples not containing agent. The blue curve corresponds to values of y calculated from the distribution of samples containing agent at 0.044 mg/m^3 .

The vertical green line is placed so the false negative rate (the fractional area under the blue curve to the left of the green line) is at the chosen PD.

The false positive rate can then be calculated (the fractional area under the red curve to the right of the green line), in this example it is 6.3×10^{-3} .

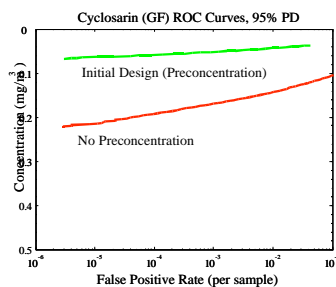
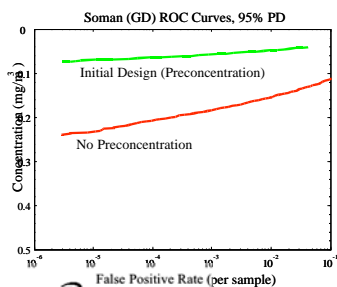
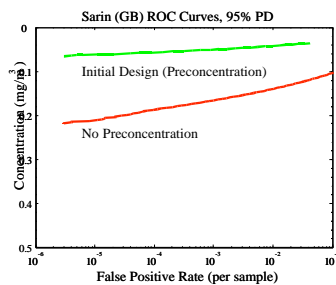
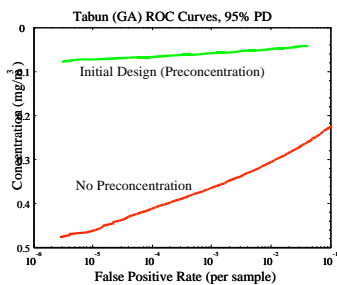
The process is then repeated at different agent concentrations.



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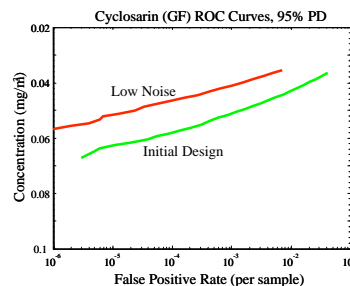
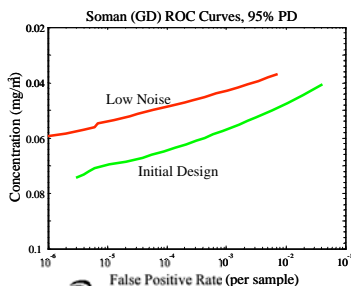
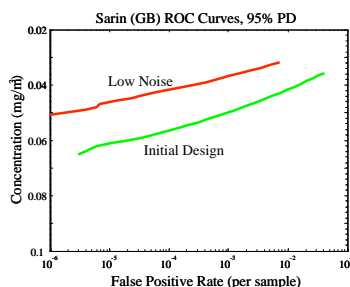
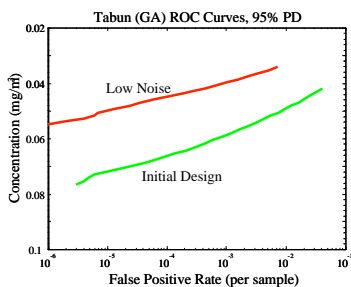
ROC Curves with and without Preconcentrator



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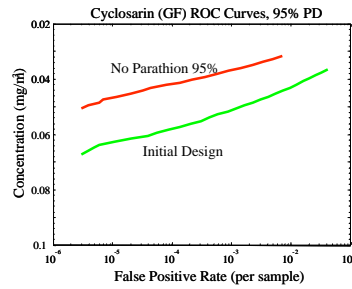
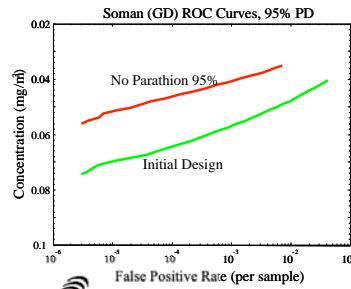
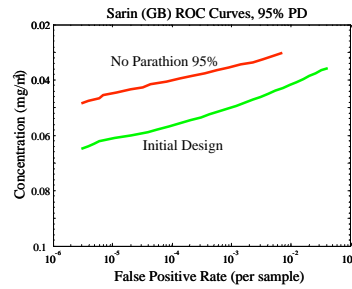
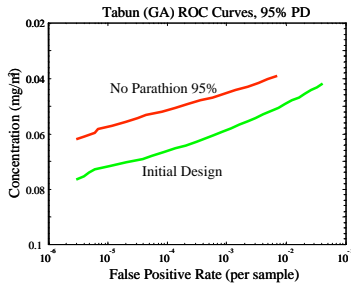
ROC Curves with Estimated and Low Noise (33% of est.)



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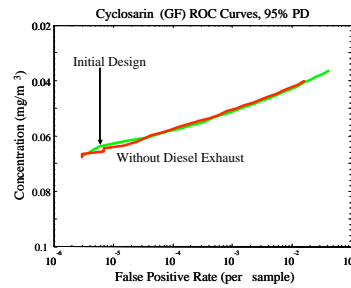
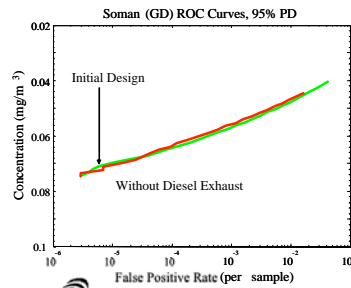
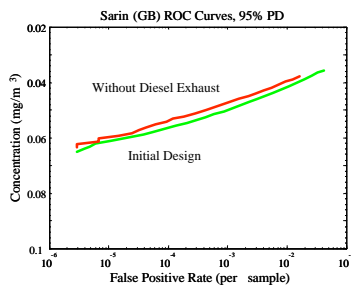
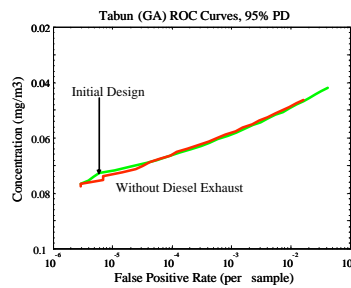
ROC Curves With and Without Parathion



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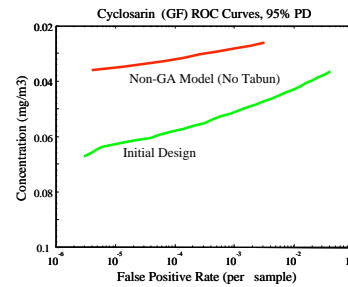
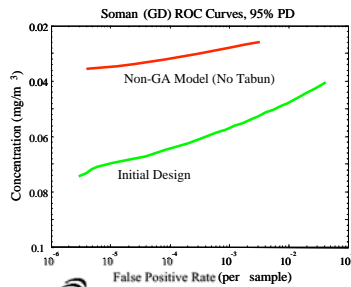
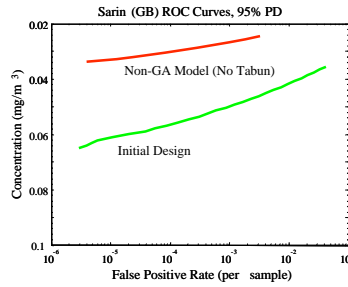
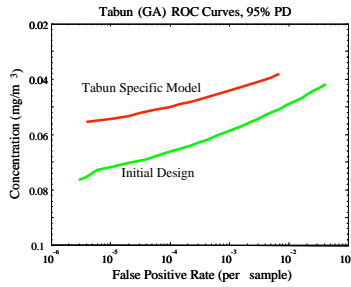
ROC Curves with and without Diesel Exhaust



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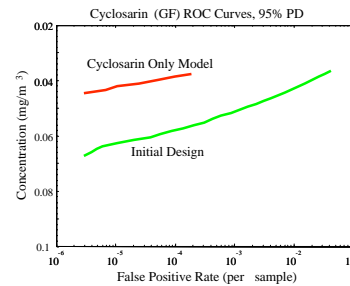
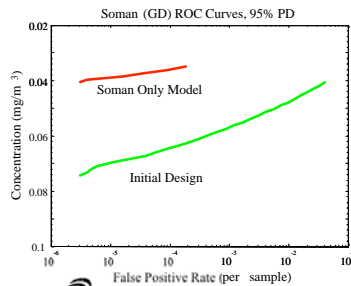
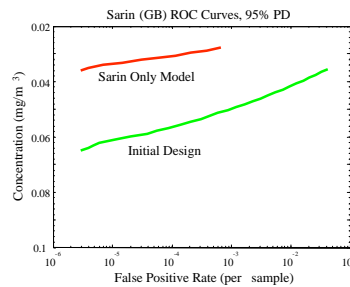
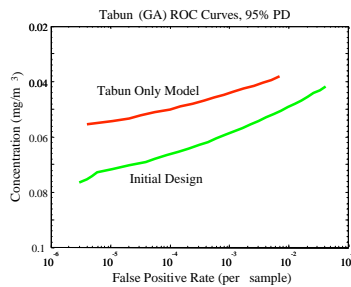
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ROC Curves for G-Agent Categories: GA & Non-GA



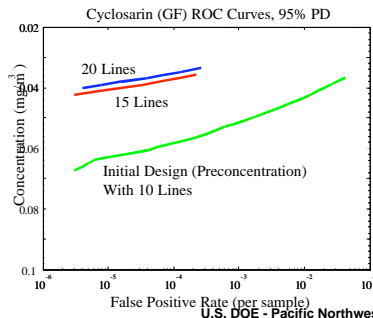
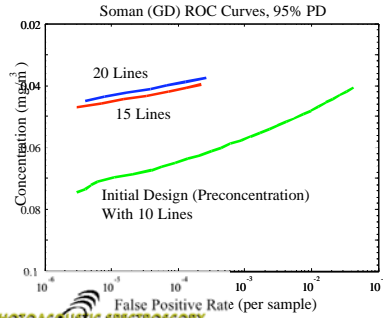
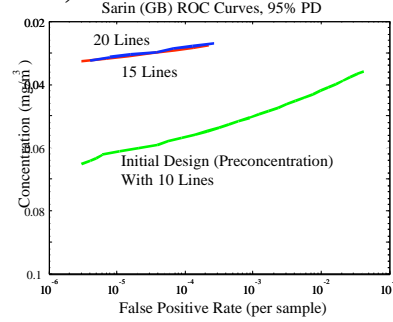
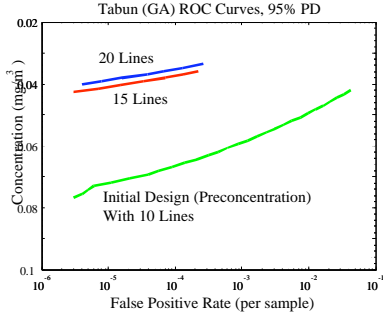
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ROC Curves for Agent Specific Models vs. Initial Design



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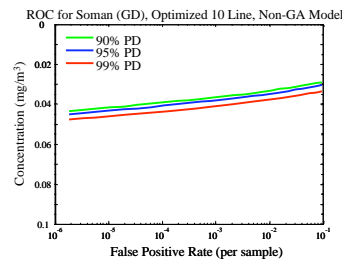
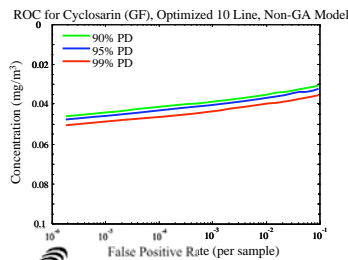
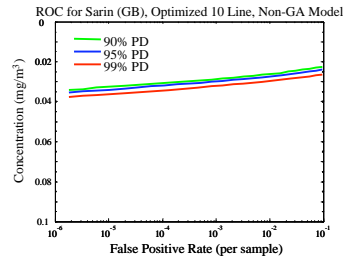
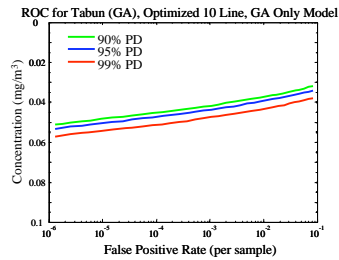
ROC Curves for G-Agents with 10, 15 & 20 laser lines



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QC L-PAS Performance is Weakly Dependent on PD ROC Curves for G-Agents: 10-Line GA and Non-GA Models: 90, 95, 99% PD

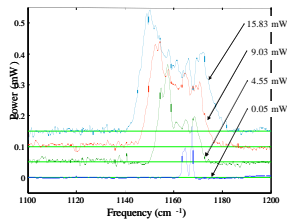


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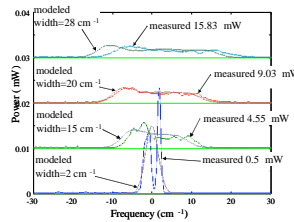
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Modeling QCL Line-shapes

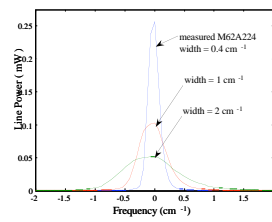
- Laser line width and shape effect the LPAS signal
- Modeling the laser line obviates expense of laser construction and testing
- Line width and shape can be explored using LPAS virtual sensor to guide:
 - Line selection
 - Laser design criteria



Measured FP-QCL Output at Different Powers



FP-QCL Output. Modeled Compared to Measured. Normalized to 1 mW.

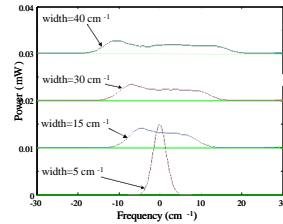
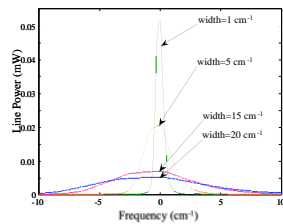
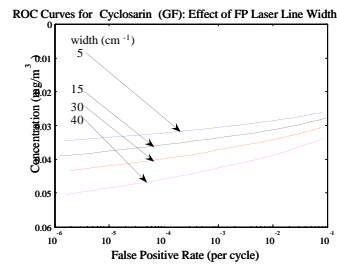
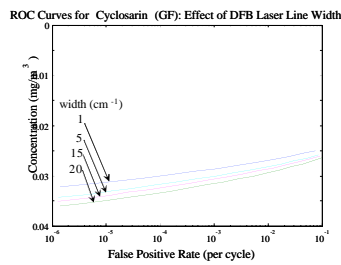


DFB-QCL Output. Modeled Curves Generated from Measured Output.



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QC L-PAS Performance Weakly Dependent on Laser Line Width ROC Curves for Cyclosarin: FP vs. DFB Line Shape



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Model Atmosphere

Concentrations for 3 typical scenarios: remote, rural, and urban*

Over 70 analytes with significant contribution to IR absorbance included in the model of ambient atmosphere (*partial list shown at right*)

Additional analytes included in battlefield scenario(s) and many analytes shown here will have different concentration ranges

Model accounts for correlation in the analyte's concentrations (*e.g. diesel exhaust components*).

Analyte	*Concentration (mg/m ³)
Water	0 - 2967
Carbon dioxide	661 - 860
Carbon monoxide	2.3 - 11.5
Methane	1.0 - 1.2
Nitric oxide	0.25 - 2.5
Nitrous oxide	0.53 - 0.65
Sulfur dioxide	0.71 - 0.87
Ozone	0.2 - 0.99
Ethane	0.00074 - 0.62
Propane	0.00073 - 0.4
Ethene	0.00081 - 0.19
Peroxyacetylnitrate	0.31 - 0.38
n-Butane	0.000048 - 0.23
Isopentane	0.0059 - 0.27
Methanol	0.047 - 0.058
Formaldehyde	0.0012 - 0.093
Nitric acid	0.065 - 0.13
Toluene	0.0011 - 0.27
Styrene	0.021 - 0.094
n-Pentane	0.0021 - 0.2
Methyl chloride	0.001 - 0.13
Acetone	0.0048 - 0.13
Isobutane	0.00072 - 0.11
Methyl chloroform	0.001 - 0.25
Acetylene	0.00075 - 0.047
Formic acid	0.034 - 0.042
Propene	0.00017 - 0.068
Isoprene	0.00056 - 0.084
Hexane	0 - 0.11
Dinitrogen pentoxide	0.06 - 0.073
Perchloroethylene	0.0002 - 0.19
Benzene	0.0029 - 0.084
Isobutene	0.0069 - 0.042
Ammonia	0.0063 - 0.0077
.....	

Information Sources.

* Finlayson -Pitts, BJ, and Pitts, JN. *Chemistry of the Upper and Lower Atmosphere*, Academic Press, San Francisco, 2000.

¹ Hobbs, PV. *Introduction to Atmospheric Chemistry*, Cambridge University Press, Cambridge, UK, 2000.

² Jacob, DJ. *Introduction to Atmospheric Chemistry*, Princeton University Press, Princeton, New Jersey, 1999.

³ Seinfeld, JH, and Pandis, SN. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley and Sons, New York, 1998.

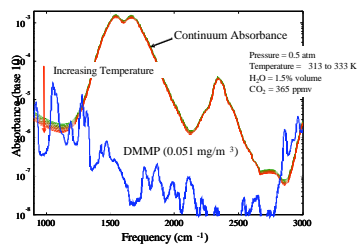
⁴ California Air Resources Board, Annual Toxics Summaries, <http://www.arb.ca.gov/adam/toxics/statesubstance.html>



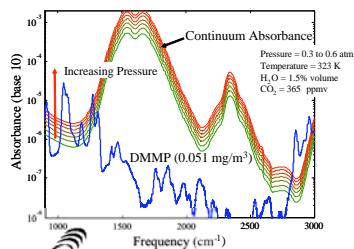
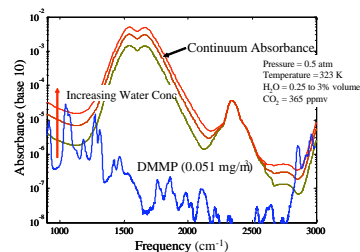
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“Real World” Modeling: IR Water Continuum

Variation of continuum absorbance with temperature



Variation of continuum absorbance with concentration



Variation of continuum absorbance with sample pressure



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Agent Detection Performance of Existing Point Detectors

Technology	Sensitivity to G-Agents	Selectivity and Probability of Detection (PD)	
IMS CAM ICAM ACADA GID	0.1 to 0.2 mg/m ³ in < 2 mins	1 On a scale of 0 to 4 (4 is best)	<ul style="list-style-type: none"> •The CAM may give false reading when used in enclosed spaces •Some vapors known to give false readings: aromatic vapors (perfumes, food flavorings, some aftershaves, peppermints, cough lozenges, and menthol cigarettes, cleaning compounds (disinfectants, methyl salicylate, menthol, etc.) smokes and fumes, and some wood preservative treatments
SAW HazMatCad CWSentry MiniCAD	<i>Fast mode: 0.3 to 0.9 mg/m³ in 20 seconds</i> Sensitive mode: 0.06 to 0.18 mg/m ³ in 2 minutes	3 On a scale of 0 to 4 (4 is best)	
<i>JSOR Rqmts</i>	0.1 mg/m ³ for G-Agents	<i>Predict Agent Categories</i>	
<i>JCAD Rqmts</i>	0.1 mg/m ³ in 30 sec. 1 mg/m ³ in 10 sec.	<i>5x 10⁻⁵ false positive rate at 90% PD</i>	
<i>LPAS BAA Goal</i>	< .007 mg/m ³	<i>10⁻⁸ False Positive Rate</i>	
QC L-PAS Initial Design	-0.04 mg/m³ with 30 second response (10 sec meas. time)	2 X 10⁻⁶ False Positive Rate at 95% PD	Initial modeling – not fully optimized

IMS: 1) National Academy of Sciences, *Strategies to Protect the Health of Deployed U.S. Forces: Detecting, Characterizing, and Documenting Exposures* (2000), Appendix D, 2) Federal Emergency Management Agency (FEMA) *Rapid Response Information System, Advantages and Limitations of Selected NBC Equipment Used by the Federal Government*
SAW: 1) Microsensor Systems *HAZMATCAD specifications*, 2) National Institutes of Justice (NIJ): *Guide for the Selection of Chemical Agent and Toxic Industrial Material Detection Equipment for Emergency First Responders*, NIJ Guide 100-00 Table 5.3



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Summary of L-PAS Results

- Performance not a strong function of laser line width
- Moderate pre-concentration improves performance considerably
- Diminishing returns on adding lines after ~15
- Diesel exhaust doesn't greatly affect performance, but parathion does
- Final system should meet required specifications for sensitivity and specificity



Example 2

- Gas Chromatography coupled with a polymer coated Surface Acoustic Wave detector
- Feasibility study
- What can be done with low GC resolution and the limits of SAW specificity?
- Reference:
 - N.B. Gallagher, B.M. Wise, J.W. Grate, **Generalized Rank Annihilation, Curve Resolution, and Target Factor Analysis Applied to Second Order Data from a Pre-separator Coupled with a Surface Acoustic Wave Array Detector**, in preparation



SAW Response Simulation

- Based on actual data, interpolated
- Polymers PIB, PVTD, OV25, PECH, OV275, BSP3
- Included non-linear effects due to surface adsorption
- Binary mixtures of TOL, MEK, PCE, BTL
- Modified data to make response less specific for analytes



GC-SAW Parameters

Run	Vapors _ Selectivity ϕ	Non-linearity Parameter ϵ	Resolution R_s δb	Noise Level S/N β
A	TOL-PCE 6-18°	-	0.05-0.5 1.2-12	33 0.01
B	TOL/MEK 55°	0-1	0.05-0.5 1.2-12	33 0.01
C	TOL/PCE 18°	-	0.05-0.5 1.2-12	2-75 0.1667-0.0044
D	TOL/BTL 38°	1	0.05-0.5 1.2-12	2-75 0.1667-0.0044
E	TOL/MEK 55°	1	0.05-0.5 1.2-12	2-75 0.1667-0.0044

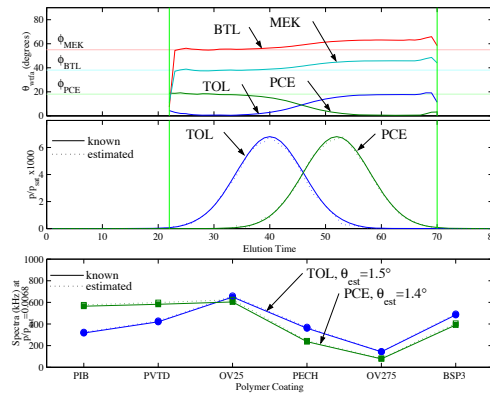


Data Analysis Methods

- TFA, Target Factor Analysis
- WTFA, Window Target Factor Analysis
- MCR, Multivariate Curve Resolution
- GRAM, Generalized Rank Annihilation Method



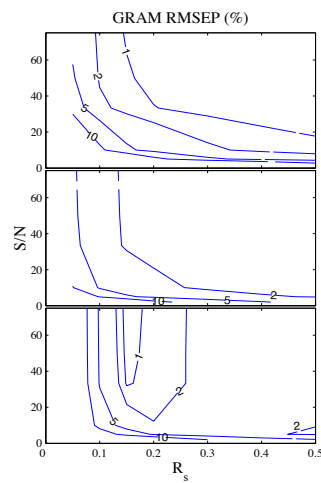
Example Response



Example WTFA and MCR for a binary mixture of TOL/PCE with $R_s=0.5$ and $S/N=33$.



Example Results from GRAM



Mixture B TOL/PCE

Mixture C TOL/BTL

Mixture D TOL/MEK



Summary of GC-SAW Results

- TFA and WTFA can provide good estimates of candidate vapors over a wide range of parameters
- MCR more sensitive to parameters than GRAM for extraction of pure component responses
- Relative RMSEP of 5% at achievable S/N and resolution as low as $R_s = 0.1$



Conclusions

- Models of complete systems enable investigation of many design parameters
- Can be used to optimize entire system to meet overall objective, not just components
- Continue to refine models as new data becomes available
- Sometimes obtain surprising results!



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